

Electronic Supplementary Information

Titanium Complexes with Octahedral Geometry Chelated by Salen Ligands Adopting β -cis Configuration for the Ring-Opening Polymerisation of Lactide

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Content

| | |
|---|----|
| Figure S1..... | P1 |
| Figure S2 | P2 |
| Figure S3. | P2 |
| Figure S4. | P3 |
| Figure S5. | P3 |
| Table S1. | P3 |
| Table S2. | P4 |
| 1 Experiments..... | P4 |
| 1.1 General | P4 |
| 1.2 Synthesis of ligands..... | P4 |
| 1.3 Synthesis of Complexes..... | P5 |
| 1.4 General procedure for lactide polymerisation..... | P6 |
| 2 References..... | P6 |

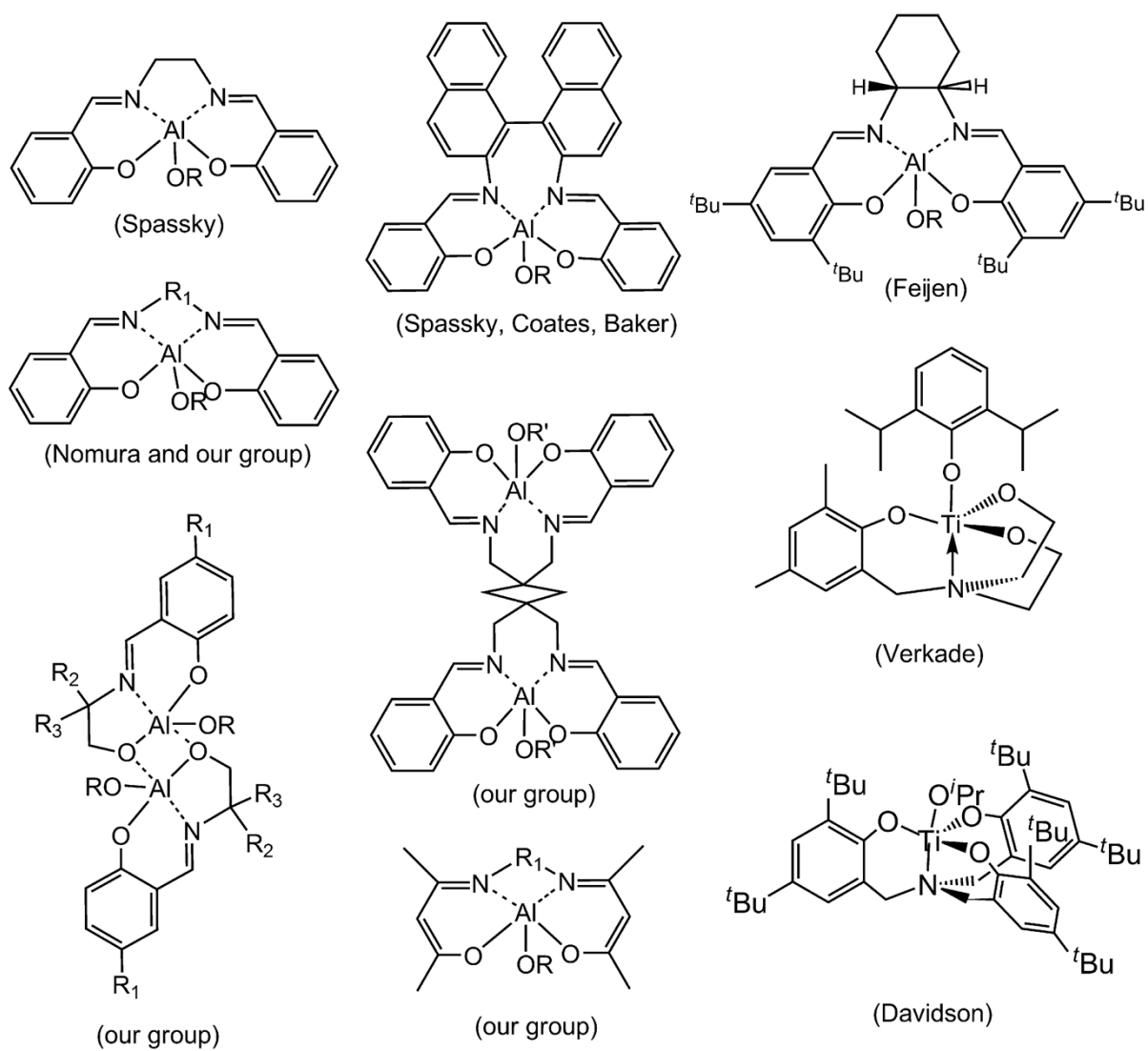


Figure S1. Some initiators for ROP of LA.

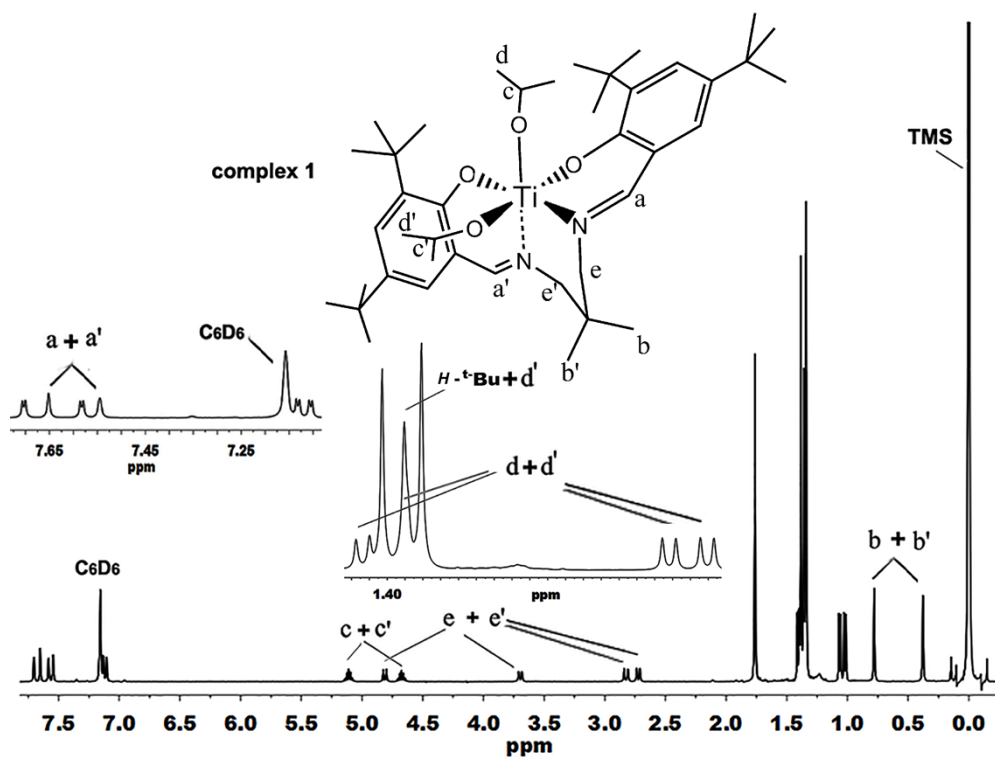


Figure S2. ^1H 400 NMR spectrum of complex **1** in C_6D_6 .

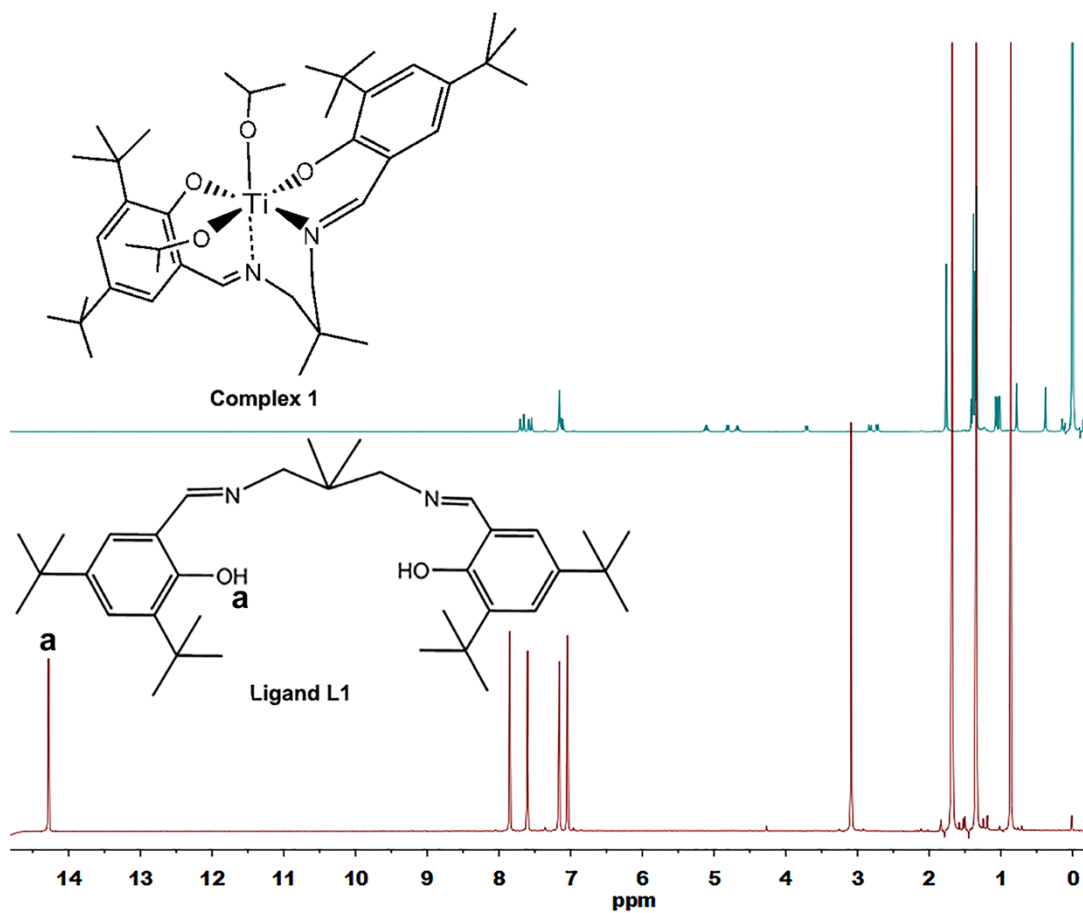


Figure S3. Stacked ^1H 400 NMR spectra of ligand **L1** and complex **1** in C_6D_6 .

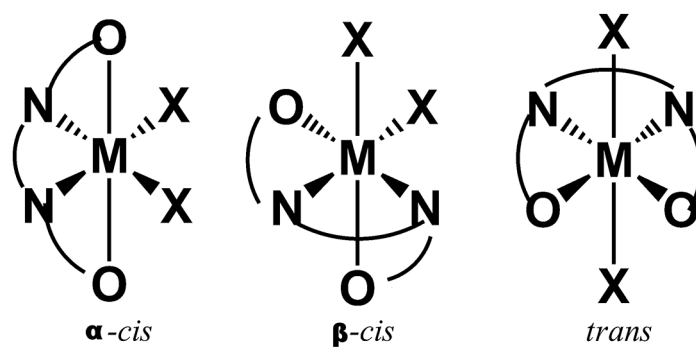


Figure S4. Possible octahedral coordination isomers.

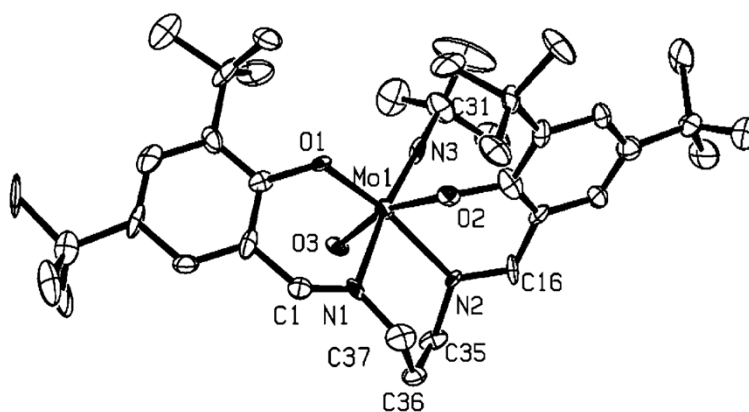


Figure S5. Crystal structure of compound **5** in reference 14.

Table S1. Selected bond lengths (Å) and angles (deg) for complex **1**.

| | | | |
|-----------|------------|-----------|------------|
| Ti1–O1 | 1.906(3) | Ti1–O2 | 1.983(3) |
| Ti1–O3 | 1.828(3) | Ti1–O4 | 1.795(3) |
| Ti1–N1 | 2.234(3) | Ti1–N2 | 2.182(3) |
| O4–Ti1–O3 | 96.04(15) | O4–Ti1–O1 | 104.67(13) |
| O3–Ti1–O1 | 96.87(13) | O4–Ti1–O2 | 89.60(14) |
| O3–Ti1–O2 | 169.42(13) | O1–Ti1–O2 | 90.32(12) |
| O4–Ti1–N2 | 95.81(13) | O3–Ti1–N2 | 90.68(13) |
| O1–Ti1–N2 | 157.23(12) | O2–Ti1–N2 | 79.82(12) |
| O4–Ti1–N1 | 173.18(14) | O3–Ti1–N1 | 84.91(12) |
| O1–Ti1–N1 | 81.88(12) | O2–Ti1–N1 | 88.44(12) |
| N2–Ti1–N1 | 77.41(12) | | |

Table S2. Details of crystal data and structure refinements for complex **1**.

| Complex | 1 |
|--|--|
| Formula | C ₄₁ H ₆₆ N ₂ O ₄ Ti |
| M | 608.86 |
| Crystal system | Monoclinic |
| Space group | C2/c |
| <i>a</i> /Å | 16.4300(12) |
| <i>b</i> /Å | 26.165(2) |
| <i>c</i> /Å | 21.2458(15) |
| <i>α</i> /° | 90 |
| <i>β</i> /° | 105.579(1) |
| <i>γ</i> /° | 90 |
| <i>V</i> /Å ³ | 8797.7(11) |
| <i>Z</i> | 8 |
| <i>T</i> /K | 188(2) |
| <i>μ</i> /mm ⁻¹ | 0.231 |
| Reflections collected | 7789 |
| Unique reflections (<i>R</i> _{int}) | 5244(0.0497) |
| GOOF | 1.059 |
| No. of parameters | 469 |
| <i>R</i> [<i>I</i> > 2σ(<i>I</i>)] | 0.0684 |
| <i>wR</i> (all data) | 0.0984 |

1 Experiments

1.1 General

All reaction with air- and water-sensitive compounds were carried out using standard Schlenk line techniques. Elemental analysis were accomplished by a Varian EL microanalyzer, ¹H NMR, ¹H-¹H COSY, ¹³C NMR and ¹H-¹³C HMQC spectra were performed on Bruker AV 300M or 400M apparatus at 25 °C in C₆D₆ and CDCl₃ for compounds and macromolecules, respectively. Crystallographic data were gathered and analyzed by referencing the reference.^{S1} The monomer conversions were confirmed by referencing the references.^{S2} Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with CHCl₃ as the eluant (flow rate: 1 mLmin⁻¹, at 35 °C). *P_r*s (the probabilities of meso linkages) were calculated from different tetrad intensities measured by homonuclear decoupled ¹H NMR^{S3}. The molecular weight was adjusted through PS standard. 3,5-di-tert-butylsalicylaldehyde, 2,2-dimethyl-1,3-propanediamine, 1,3-propanediamine, 3,5-dichlorosalicylaldehyde, salicylaldehyde and titanium tetraisopropoxide was obtained from Aldrich.

1.2 Synthesis of ligands

Ligands **1** – **4** were synthesized by published procedures. ^{S1a, S2b}

1.3 Synthesis of Complexes

General process: A mixture of ligand **Ln** (**n=1, 2, 3** or **4**, 2.5 mmol) and titanium tetraisopropoxide (2.5 mmol) in 20 mL toluene was stirred for ca. 24 h at 25 °C in glovebox. And concentrated to ca. 2.0 mL to give a yellow powder, then the product was washed with about 0.5 mL of dry pentane and dried in vacuum. The product was isolated as yellow solid in 83.4 – 94.7% yields.

Complex 1: ¹H NMR (400 MHz, C₆D₆) δ 7.70 (2s, 1H, ArH), 7.65 (s, 1H, N=CH), 7.58 (2s, 1H), 7.54 (s, 1H, N=CH), 7.13 (2s, 1H, ArH), 7.11 (2s, 1H, ArH), 5.11 (2t, *J* = 12.1, 6.0 Hz, 1H, OCH(CH₃)₂), 4.81 (2s, 1H, CH₂), 4.67 (2t, *J* = 12.1, 6.1 Hz, 1H, OCH(CH₃)₂), 3.70 (2s, 1H, CH₂), 2.82 (2s, 1H, CH₂), 2.72 (2s, 1H, CH₂), 1.41 (d, *J* = 6.1 Hz, 3H, OCH(CH₃)₂), 1.76 (s, 9H, C(CH₃)₃), 1.38 (s, 9H, C(CH₃)₃), 1.35 (bs, 12H, 9 H, C(CH₃)₃ and 3H, OCH(CH₃)₂), 1.34 (s, 9H, C(CH₃)₃), 1.06 (d, *J* = 6.1 Hz, 3H, OCH(CH₃)₂) 1.02 (d, *J* = 6.1 Hz, 3H, OCH(CH₃)₂), 0.78 (s, 3H, C-CH₃), 0.38 ppm (s, 3H C-CH₃). ¹³C NMR (100 MHz, C₆D₆) δ 165.74 (ArC), 164.67 (N=CH), 164.11 (ArC), 162.09 (N=CH), 139.09 (ArC), 139.00 (ArC), 137.23 (ArC), 137.14 (ArC), 129.37 (ArC), 128.77 (ArC), 126.40 (ArC), 125.70 (ArC), 123.83 (ArC), 121.94 (ArC), 77.63 (OCH(CH₃)₂), 76.59 (CH₂), 73.19 (OCH(CH₃)₂), 72.54 (CH₂), 36.89 (C(CH₃)₃), 35.80 (C(CH₃)₃), 35.25 (C(CH₃)₃), 34.10 (C(CH₃)₃), 31.80 (C(CH₃)₃), 31.69 (C(CH₃)₃), 30.48 (C(CH₃)₃), 30.19 (C(CH₃)₃), 27.09 (OCH(CH₃)₂), 26.76 (OCH(CH₃)₂), 26.20 (OCH(CH₃)₂), 26.14 (OCH(CH₃)₂), 26.10 (C-CH₃), 23.47 ppm (C-CH₃). Anal. Calcd for C₄₁H₆₄N₂O₄Ti (%): C, 70.47; H, 9.52; N, 4.01. Found: C, 70.49; H, 9.55; N, 4.04. Crystal of **1** suitable for X-ray structural analyses was grown in benzene solution. CCDC: 908773.

Complex 2: ¹H NMR (400 MHz, C₆D₆) δ 7.72 (2d, *J* = 13.5, 6.7 Hz, 2H, ArH), 7.65 (s, 1H, N=CH), 7.60 (2d, *J* = 13.2, 6.6 Hz, 2H, ArH), 7.55 (s, 1H, N=CH), 7.19 – 7.13 (m, 4H, ArH), 5.13 (2t, *J* = 12.2, 6.1 Hz, 1H, OCH(CH₃)₂), 4.84 (2s, 1H, CH₂), 4.69 (2t, *J* = 12.1, 6.0 Hz, 1H, OCH(CH₃)₂), 3.72 (2s, 1H, CH₂), 2.84 (2s, 1H, CH₂), 2.73 (2s, 1H, CH₂), 1.44 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂), 1.37 (s 3H, OCH(CH₃)₂), 1.08 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂) 1.03 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂), 0.79 (s, 3H, C-CH₃), 0.40 ppm (s, 3H C-CH₃). ¹³C NMR (100 MHz, C₆D₆) δ 166.58 (ArC), 165.07 (N=CH), 164.77 (ArC), 162.97 (N=CH), 140.03 (ArC), 139.57 (ArC), 138.11 (ArC), 137.86 (ArC), 129.94 (ArC), 129.03 (ArC), 127.22 (ArC), 126.14 (ArC), 124.37 (ArC), 122.55 (ArC), 77.83 (OCH(CH₃)₂), 76.79 (CH₂), 73.84 (OCH(CH₃)₂), 73.12 (CH₂), 27.90 (OCH(CH₃)₂), 27.23 (OCH(CH₃)₂), 27.09 (OCH(CH₃)₂), 27.01 (OCH(CH₃)₂), 26.75 (C-CH₃), 24.27 ppm (C-CH₃). Anal. Calcd for C₂₅H₂₄N₂O₄Ti (%): C, 63.29; H, 7.22; N, 5.90. Found: C, 63.27; H, 7.19; N, 5.87.

Complex 3: ¹H NMR (400 MHz, C₆D₆) δ 7.74 (2s, 1H, ArH), 7.68 (s, 1H, N=CH), 7.62 (2s, 1H), 7.57 (s, 1H, N=CH), 7.18 (2s, 1H, ArH), 7.15 (2s, 1H, ArH), 5.15 (2t, *J* = 12.0, 6.0 Hz, 1H, OCH(CH₃)₂), 4.86 (2s, 1H, CH₂), 4.71 (2t, *J* = 12.0, 6.0 Hz, 1H, OCH(CH₃)₂), 3.73 (2s, 1H, CH₂), 2.86 (2s, 1H, CH₂), 2.75 (2s, 1H, CH₂), 1.45 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂), 1.39 (s 3H, OCH(CH₃)₂), 1.10 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂) 1.05 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂), 0.81 (s, 3H, C-CH₃), 0.42 ppm (s, 3H C-CH₃). ¹³C NMR (100 MHz, C₆D₆) δ 167.20 (ArC), 166.14 (N=CH), 165.95 (ArC), 164.03 (N=CH), 141.12 (ArC), 140.98 (ArC), 139.30 (ArC), 139.02 (ArC), 131.03 (ArC), 130.54 (ArC), 128.36 (ArC), 127.53 (ArC), 125.79 (ArC), 123.88 (ArC), 79.23 (OCH(CH₃)₂), 78.01 (CH₂), 75.07 (OCH(CH₃)₂), 74.30 (CH₂), 29.02 (OCH(CH₃)₂), 28.57 (OCH(CH₃)₂), 28.31 (OCH(CH₃)₂), 28.19 (OCH(CH₃)₂), 28.00 (C-CH₃), 25.39 ppm

(C-CH₃). Anal. Calcd for C₂₅H₃₀ C₁₄N₂O₄Ti (%): C, 49.05; H, 4.94; N, 4.58. Found: C, 49.01; H, 4.90; N, 4.56.

Complex 4: ¹H NMR (400 MHz, C₆D₆) δ 7.71 (2s, 1H, ArH), 7.62 (s, 1H, N=CH), 7.60 (2s, 1H, ArH), 7.54 (s, 1H, N=CH), 7.06 (2s, 1H, ArH), 7.05 (2s, 1H, ArH), 5.02 (2t, *J* = 12.1, 6.0 Hz, 1H, OCH(CH₃)₂), 4.80 – 4.68 (m, 2H, OCH(CH₃)₂ and CH₂), 3.70 – 3.57 (m, 1H, CH₂), 3.55 – 3.45 (m, 1H, CH₂), 3.40 – 3.30 (m, 1H, CH₂), 3.17 (t, *J* = 9.3 Hz, 1H, CH₂), 3.06 – 2.92 (m, 1H, CH₂), 1.79 (s, 9H, C(CH₃)₃), 1.43 (s, 9H, C(CH₃)₃), 1.36 (s, 9H, C(CH₃)₃), 1.35 (s, 9H, C(CH₃)₃), 1.29 (d, *J* = 6.1 Hz, 3H, OCH(CH₃)₂), 1.09 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂), 1.04 (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂), 0.95 ppm (d, *J* = 6.0 Hz, 3H, OCH(CH₃)₂). ¹³C NMR (100 MHz, C₆D₆) δ 165.58 (ArC), 165.32 (N=CH), 163.22 (ArC), 161.83 (N=CH), 138.94 (ArC), 138.86 (ArC), 137.19 (ArC), 137.08 (ArC), 129.33 (ArC), 128.75 (ArC), 126.73 (ArC), 126.16 (ArC), 123.18 (ArC), 121.72 (ArC), 78.13 (OCH(CH₃)₂), 77.60 (CH₂), 76.51 (OCH(CH₃)₂), 60.55 (CH₂), 60.16 (CH₂), 35.73 (C(CH₃)₃), 35.38 (C(CH₃)₃), 34.19 (C(CH₃)₃), 34.08 (C(CH₃)₃), 31.75 (C(CH₃)₃), 30.82 (C(CH₃)₃), 30.50 (C(CH₃)₃), 30.15 (C(CH₃)₃), 29.74 (OCH(CH₃)₂), 26.95 (OCH(CH₃)₂), 26.12 (OCH(CH₃)₂), 26.45 (OCH(CH₃)₂), 26.12 ppm (OCH(CH₃)₂). Anal. Calcd for C₃₉H₆₂N₂O₄Ti (%): C, 69.83; H, 9.32; N, 4.18. Found: C, 69.80; H, 9.29; N, 4.15.

1.4 General procedure for lactide polymerisation

1.4.1 Polymerisations of lactide in solution.

In a representational polymerisation reaction, titanium complex (0.5 mmol) and the required quantity of lactides dried by 4A molecular sieves in advance in toluene (100 mL) were loaded in a flame-dried vessel containing a magnetic bar. The ampulla was immersed in an oil bath at 100 °C. After a certain reaction time, the polymer was isolated by precipitating with cold methanol or refrigerated centrifuge. The solid was collected and dried in vacuo at 35°C for 40 h.

1.4.2 Melt polymerisations of lactide.

In a representational melt polymerisation reaction, titanium complex (0.05 mmol) and lactides (15 mmol, 2.16 g) were loaded in a flame-dried vessel containing a magnetic bar. The ampulla was immersed in an oil bath at 150 °C for 2 h before being cooled to RT. Methanol (20 mL) was added and the solid was dissolved in dichloromethane. The solvents were removed in vacuo and the solid was washed with methanol (50 mL×3) to remove residual monomer. The solid was collected and dried in vacuo at 35°C for 40 h.

2 References

- S1 (a) Z. H. Tang, X. S. Chen, X. Pang, Y. K. Yang, X. F. Zhang, X. B. Jing, *Biomacromolecules* 2004, **5**, 965–970. (b) X. Pang, H. Z. Du, X. S. Chen, X. Wang, X. B. Jing, *Chem. –Eur. J.* 2008, **14**, 3126–3136. (c) G. M. Sheldrick, SHELXTL, Version 5. 1, Siemens Industrial Automation, Inc., 1997.
- S2 (a) Z. H. Tang, X. S. Chen, Y. K. Yang, X. Pang, J. R. Sun, X. F. Zhang, X. B. Jing, *J Polym Sci Part A: Polym Chem.* 2004, **42**, 5974–5982. (b) H. Du, A. H. Velders, P. J. Dijkstra, Z. Y. Zhong, X. S. Chen, J. Feijen, *Macromolecules* 2009, **42**, 1058–1066.

S3 B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* 2001, **123**, 3229–3238.